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A GENERAL ROUTE TO TERMINALLY SUBSTITUTED ALLYLIC DERIVATIVES O--ETC(U)
JUN 77 D SEYFERTH, K R WURSTHORN N00014-76-C-0837

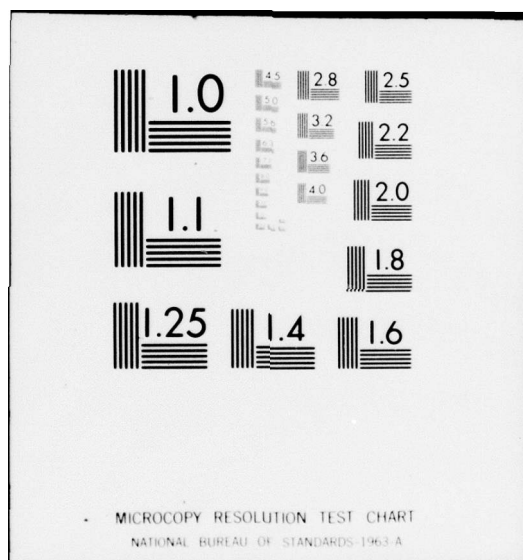
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A General Route to Terminally Substituted Allylic Derivatives
of Silicon and Tin. Preparation of Allylic Lithium Reagents.

by

Dietmar Seyferth, Karl R. Wursthorn

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Prepared for Publication

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Massachusetts Institute of Technology
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A General Route to Terminally Substituted Allylic Derivatives
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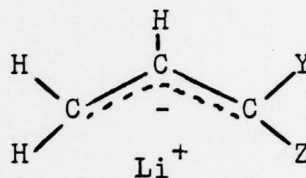
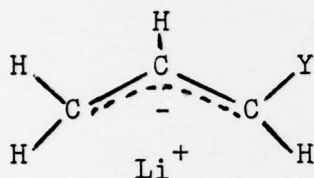
Abstract.

Wittig reactions of the appropriate β -trimethylstannyl and β -trimethylsilyl-ethyltriphenylphosphonium salt-derived ylides ($\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$, $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SiMe}_3$, $\text{Ph}_3\text{P}=\text{C}(\text{Me})\text{CH}_2\text{SiMe}_3$ in the examples presented) with aldehydes and ketones provide a useful, general route to allylic compounds of silicon and tin. The required phosphonium salts are readily prepared by alkylation of phosphorus ylides with $\text{Me}_3\text{SnCH}_2\text{I}$ and $\text{Me}_3\text{SiCH}_2\text{I}$. The allylic tin compounds thus prepared were converted to the respective allylic lithium reagents in high yield by transmetalation with methyllithium in tetrahydrofuran.

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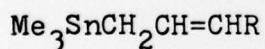
Sir:

We have reported recently concerning the synthesis and the unusual regioselectivity of gem-dichloroallyllithium in carbonyl addition reactions.¹ The results of this study prompted further interest in unsymmetrically substituted allyllithium reagents of general types 1 and 2. Three major routes are available for the

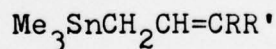


synthesis of allylic lithium reagents: direct lithiation of olefins,² allyl ether cleavage with metallic lithium,³ and transmetalation reactions of allylic derivatives of heavy metals, principally of tin and lead.^{1,4}

We describe here a new, general route to allylic derivatives of tin of types 3 and 4. These are useful starting materials for



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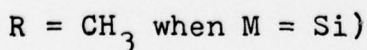
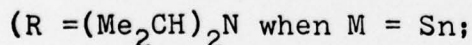
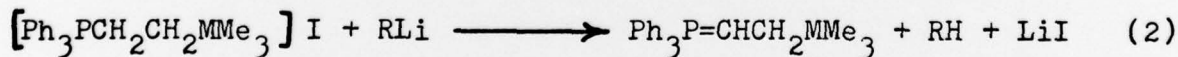
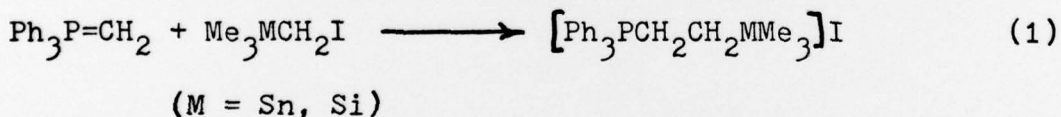
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allylic lithium reagents of types 1 and 2, where Y and Z = alkyl and aryl. Our new allyltin synthesis has added importance in view of the newly developed utility of the allyltin^{compounds} themselves in organic and organometallic synthesis.⁵ Furthermore, this general procedure can be extended to the synthesis of allylsilicon compounds analogous to 3 and 4, and, although this has not yet been examined, also of allyl compounds of germanium and lead. This is of interest,

since allylsilanes also have found useful applications in organic synthesis in recent years.⁶

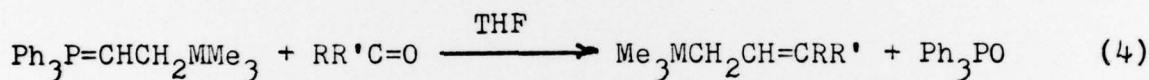
The general concept involved in our allylmetallics synthesis is based on an allyltin preparation of Hannon and Traylor.⁷ These workers used the reaction of trimethyltinlithium with vinyltriphenylphosphonium bromide to prepare the ylide $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$, which could be used in a Wittig reaction with cyclohexanone.⁸ In our hands, however, this procedure gave only moderate yields of the expected allyltin compound, $\text{Me}_3\text{SnCH}_2\text{CH}=\text{C}_6\text{H}_{10}$ -cyclo (44%, Wittig reaction at -93° ; 48%, at room temperature), based on the 1:1 $\text{Me}_3\text{SnLi}/[\text{Ph}_3\text{PCH}=\text{CH}_2]\text{Br}$ stoichiometry used, and, moreover, a considerable portion ($\sim 50\%$) of the trimethyltinlithium was converted to hexamethylditin during the course of the reaction.

Our new procedure uses the same Wittig reagent but involves a different preparation, as shown in eq. 1 and 2. The phosphonium

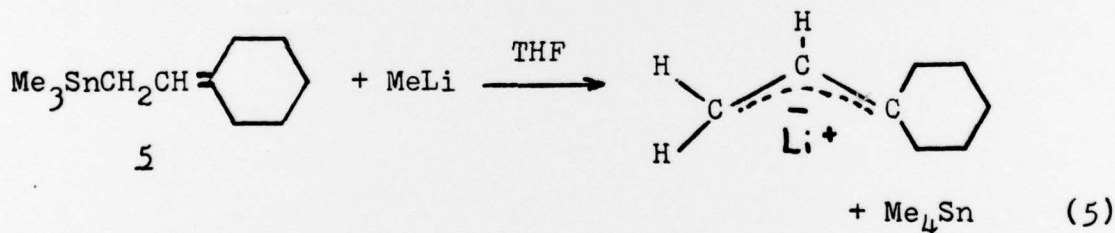


halides, $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{SnMe}_3]\text{I}$ and $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{SiMe}_3]\text{I}$, were isolated in better than 85% yield and were fully characterized. That this procedure is extendable to the synthesis of $[\text{Ph}_3\text{PCH}(\text{R})\text{CH}_2\text{MMe}_3]\text{I}$ salts was demonstrated by the preparation of $[\text{Ph}_3\text{PCH}(\text{Me})\text{CH}_2\text{SiMe}_3]\text{I}$ by reaction of $\text{Ph}_3\text{P}=\text{CHCH}_3$ with $\text{Me}_3\text{SiCH}_2\text{I}$. This procedure is simple and easily carried out. The preparation of the required phosphorus

Methylolithium serves well as the base in the case of $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{-SiMe}_3]\text{I}$ and $[\text{Ph}_3\text{PCH}(\text{CH}_3)\text{CH}_2\text{SiMe}_3]\text{I}$, but for the deprotonation of $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{SnMe}_3]\text{I}$, lithium amides, R_2NLi ($\text{R} = \text{Me}_2\text{CH}$ or Me_3Si), must be used since organolithium reagents do not react regio-specifically, attacking in part at tin as well as at the protons α to phosphorus. The ylides formed, $\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$, $\text{Ph}_3\text{P}=\text{CH-CH}_2\text{SiMe}_3$ and $\text{Ph}_3\text{P}=\text{C}(\text{Me})\text{CH}_2\text{SiMe}_3$, react readily with aldehydes and, in general, somewhat less well with ketones, to give the expected allylstannanes and allylsilanes (eq. 4; Table 1).



The three allylic tin compounds in Table 1 undergo ready conversion to the respective allylic lithium reagents, e.g., eq. 5.



In a typical reaction, 5 (3.74 mmol) in 200 ml of dry THF at 0° , under nitrogen, was treated with 4.1 mmol of methylolithium in diethyl ether. The resulting yellow solution was stirred for 30 min. at 0° and then 20 mmol of acetone was added. After the reaction mixture had been stirred at room temperature for 30 min., hydrolytic work-up was followed by GLC analysis of the organic phase to establish the presence of 6 in 89% yield. The results of these

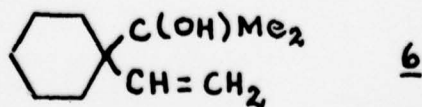


TABLE 1. Preparation of Allylic Silicon and Tin Compounds.^a



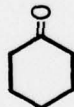


Ylide Reagent	Carbonyl Reactant	Allylic Product (% Yield)	trans/cis Ratio
$\text{Ph}_3\text{P}=\text{CHCH}_2\text{SnMe}_3$	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{O}$	$\text{Me}_3\text{SnCH}_2\text{CH}=\text{CHC}_6\text{H}_{13}\text{-n}$ (98)	70/30
		$\text{Me}_3\text{SnCH}_2\text{CH}=\text{CH}$  (79)	
	$\text{C}_6\text{H}_5\text{CH}=\text{O}$	$\text{Me}_3\text{SnCH}_2\text{CH}=\text{CHC}_6\text{H}_5$ (70)	95/5
	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{O}$	$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHC}_6\text{H}_{13}\text{-n}$ (71)	75/25
$\text{Ph}_3\text{P}=\text{CHCH}_2\text{SiMe}_3$		$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}$  (85)	
	$\text{C}_6\text{H}_5\text{CH}=\text{O}$	$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHC}_6\text{H}_5$ (63)	64/36
	$(\text{C}_2\text{H}_5)_2\text{C}=\text{O}$	$\text{Me}_3\text{SiCH}_2\text{CH}=\text{C}(\text{C}_2\text{H}_5)_2$ (38) ^b	
	$(\text{CF}_3)_2\text{C}=\text{O}$	$\text{Me}_3\text{SiCH}_2\text{CH}=\text{C}(\text{CF}_3)_2$ (43)	
$\text{Ph}_3\text{P}=\text{C}(\text{CH}_3)\text{CH}_2\text{SiMe}_3$	$\text{C}_2\text{H}_5\text{CH}=\text{O}$	$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CHC}_2\text{H}_5$ (74)	55/45 ^c
	$\text{C}_6\text{H}_5\text{CH}=\text{O}$	$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CHC}_6\text{H}_5$ (72)	50/50
		(deprotonation regenerated the starting phosphonium salt)	

TABLE 1. Footnotes

- ^a Reactions were carried out in THF medium. The reactants were mixed at room temperature and the reaction mixture was stirred and heated at reflux under nitrogen for 12-15 hr. Trap-to-trap distillation at 0.05-0.1 mm into a receiver cooled to -78° gave a solution of the product which was analyzed by GLC. In larger preparative-scale reactions the product was isolated by vacuum distillation.
- ^b The procedure in (a) gave only a yield of 27%. In this reaction the THF solvent was replaced by toluene and the reaction mixture then was heated at reflux for 40 hr.
- ^c Stereochemistry was not assigned.

experiments are illustrated in Charts 1, 2 and 3. The product yields are uniformly excellent. A discussion of the observed regioselectivities in the reactions of these ambident reagents will be deferred until this study has been completed.

It is obvious that this new route to allylic compounds of silicon and tin should be quite general in its scope of applicability. By appropriate variation of the phosphorus ylide and the carbonyl substrate in these reactions, allylic derivatives of silicon and tin of type $\text{Me}_3\text{MCH}_2\text{C(R)=CR'R''}$, where R, R' and R'' should be capable of wide variation, should be accessible. The allyltins thus prepared would provide starting materials for many new allylic lithium reagents. In many cases the direct lithiation procedure, the reaction of RLi/Lewis base or $\text{RLi/Me}_3\text{OK}$ with an appropriate unsaturated hydrocarbon, would provide the simplest route to the desired allylic lithium reagent.² However, the additives which usually are required to effect such metalations may not always be compatible with other functionality in the carbonyl reactant or may interfere in other ways. Also, there will be instances when the appropriate unsaturated hydrocarbon is not available. Thus the versatility of our new procedure and its ease of application may prove very useful in organic and organometallic synthesis.

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CHART 1. Reactions of n-Hexylallyllithium

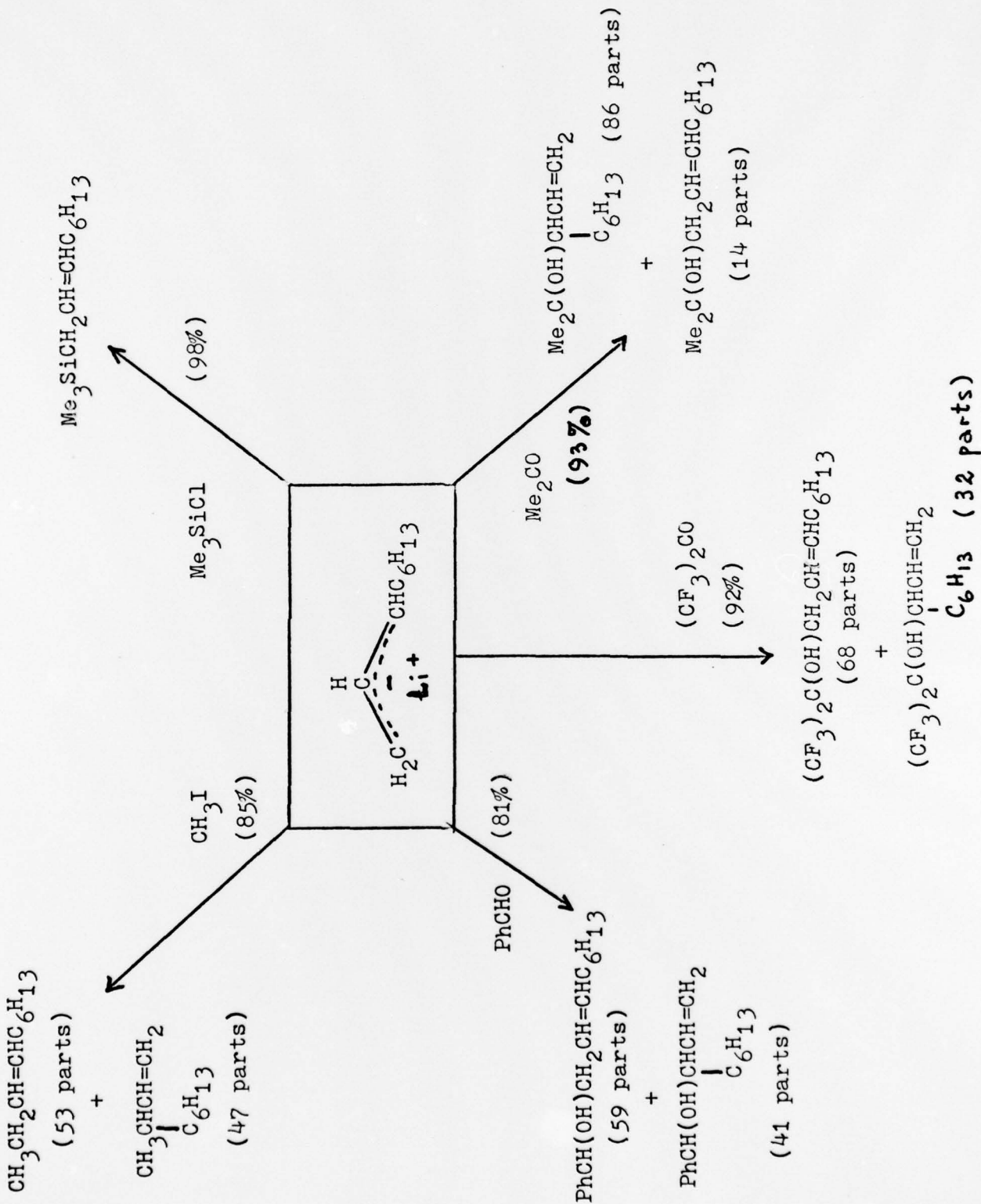


CHART 2. Reactions of 1,1-Cyclopentamethyleneallyllithium

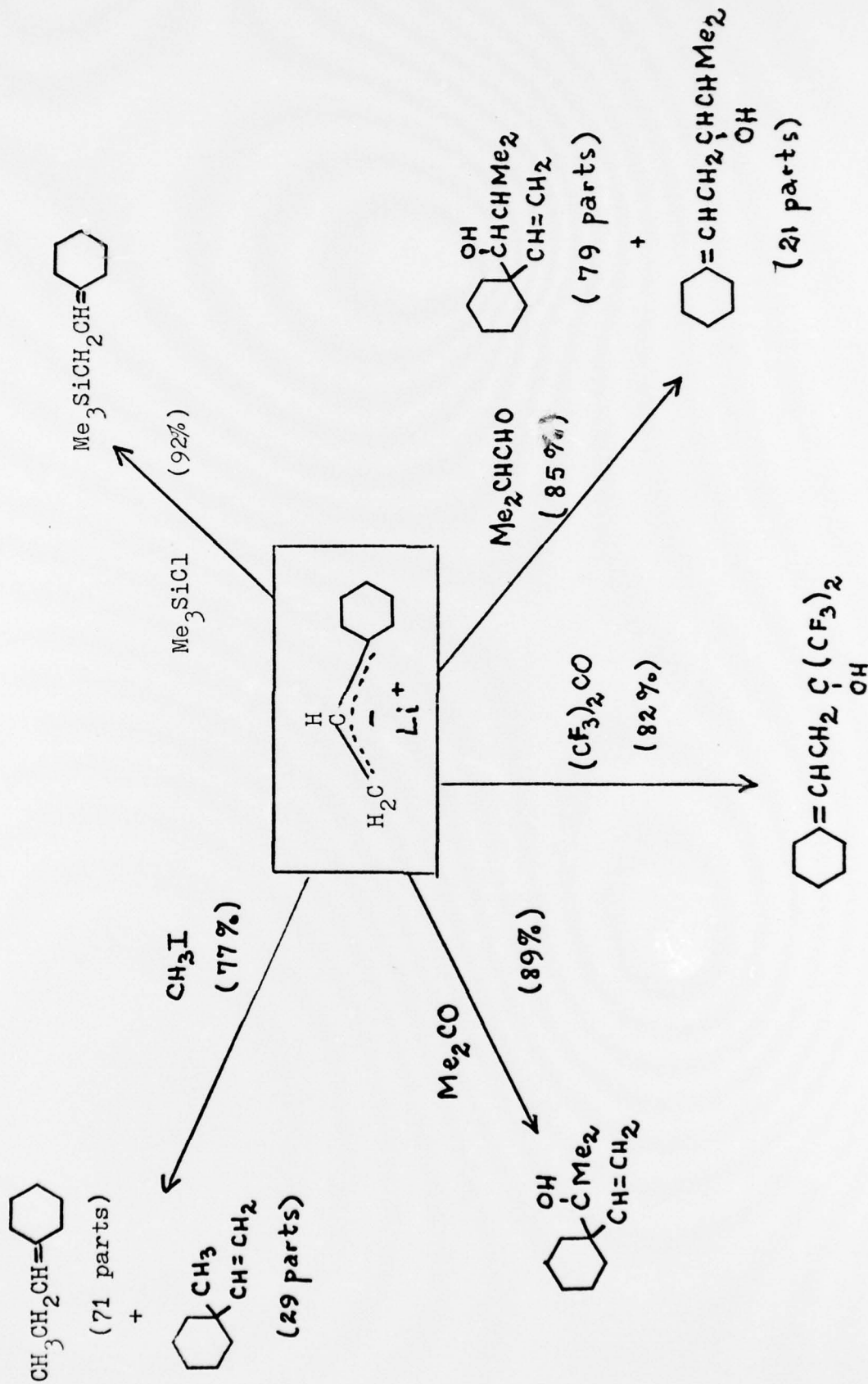
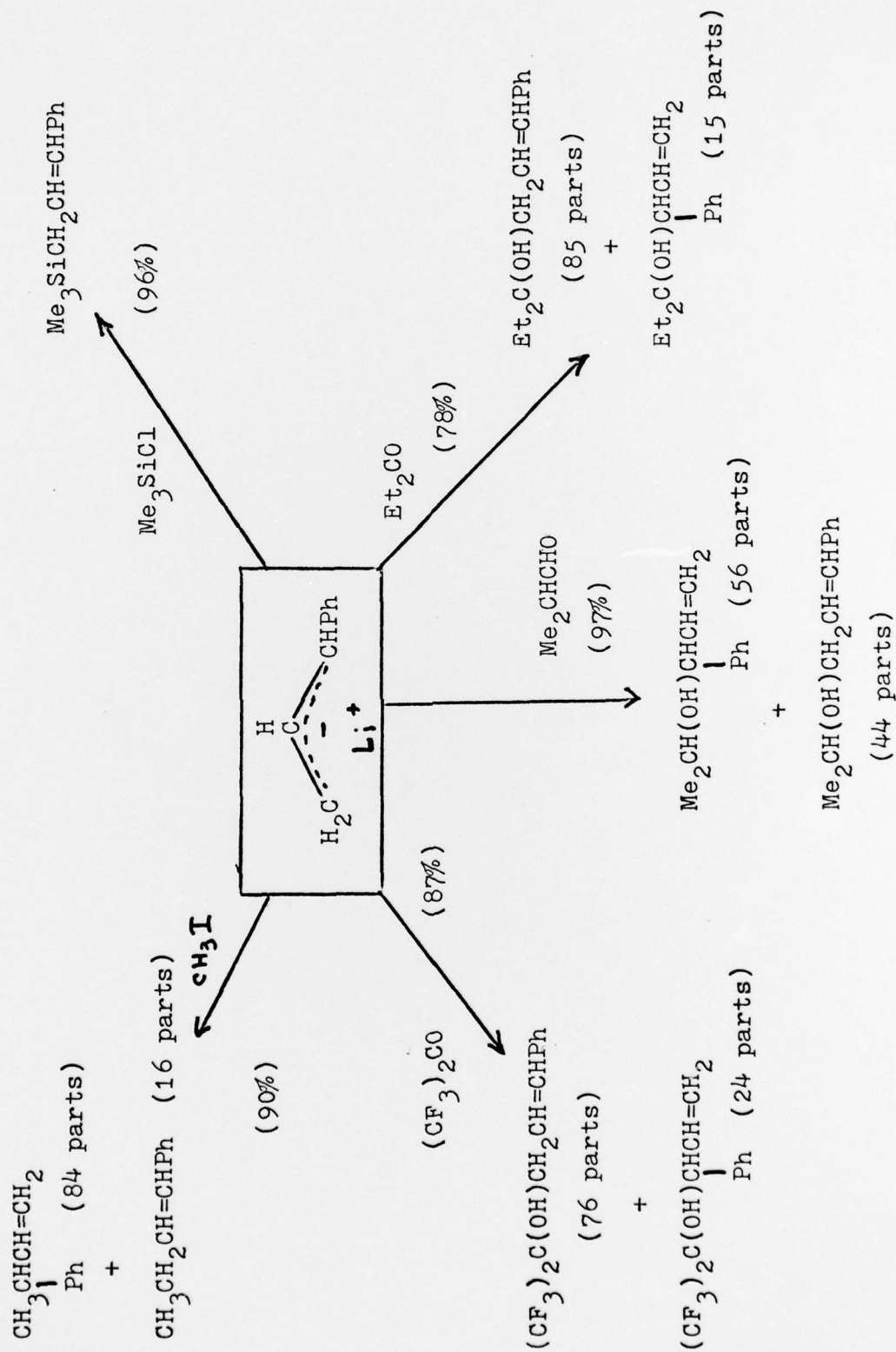


CHART 3. Reactions of Phenylallyllithium.



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